THE ROLE OF pH, TEMPERATURE AND CATALYST TYPE IN CARAMEL MANUFACTURING PROCESS

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ABSTRACT

Caramel is a brown to black liquid or solid having the characteristic odor of burn sugar and a pleasant bitter taste. It is prepared by heat treatment of carbohydrate in a process called caramelization. The purpose of this study is to investigate the effect of temperature, pH, types of catalyst and also time taken to complete caramelization process for glucose. In this research, glucose was used to prepare two different classes of caramel (class III and class IV). Class III is prepared by adding ammonia to glucose and class IV by adding ammonia and sodium sulfite to glucose. Different preheating temperature ranged between (70-100)°C and different pH values ranged between (5-9) were investigated to find the optimum preheating temperature and pH values for caramelization reaction at 121°C. The prepared caramel was characterized by measuring its absorbance using UV-VIS spectrophotometer at wavelength 510 nm and 610 nm. The higher absorbance reading was at preheating temperature 100°C for both Ammonia and Ammonia Sulfite caramel. Result from the experiment showed that at alkaline condition, pH 8 give better results for both Ammonia and Ammonia Sulfite caramel compare to other pH. It also showed that Ammonia Sulfite caramel, at same condition with Ammonia caramel have darker color and higher absorbance reading.

ABSTRAK

Karamel adalah berwarna coklat gelap hingga hitam samaada dalam bentuk cecair ataupun pepejal. Karamel disediakan dengan memanaskan karbohidrat pada suhu tertentu dalam proses yang dipanggil pengkaramelan. Tujuan kajian ini ialah untuk menyiasat kesan suhu, pH, pemangkin dan juga masa yang diambil untuk menyelesaikan pengkaramelan proses untuk glukosa. Dalam kajian ini, glukosa digunakan untuk menyediakan dua jenis karamel dari kelas yang berbeza (kelas III dan kelas IV). Kelas III disediakan dengan menambah ammonia ke dalam larutan glukosa manakala kelas IV pula dengan menambah ammonia dan natrium sulfit ke dalam larutan glukosa. Suhu pemanasan yang berbeza diantara (70-100)°C dan nilai pH yang berbeza diantara (5-9) dikaji untuk mendapatkan suhu dan pH yang optimum bagi proses pengkaramelan pada suhu 121°C. Karamel yang sudah disediakan diukur dengan menggunakan spektrofotometer UV-VIS pada gelombang 510 nm dan 610 nm. Pada suhu 100°C, serapannya adalah lebih tinggi berbanding pada suhu lain untuk kedua-dua ammonia caramel dan ammonia sulfite karamel. Hasil daripada eksperimen menunjukkan pada keadaan alkali, pH 8 memberi keputusan lebih baik untuk kedua-dua Ammonia dan karamel Ammonia Sulfite berbandingan pH lain. Ia juga menunjukkan ammonia sulfit karamel, pada keadaan sama dengan ammonia caramel mempunyai warna lebih gelap dengan bacaan serapan yang lebih tinggi.

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LIST OF ABBREVIATIONS

HMW	=	High molecular weight
LMW	=	Low molecular weight
HMF	=	Hydroxymethyl-furaldehyde
THI	=	Tetrahydroxybuthyl imidazole
MeI	=	Methylimidazole
ABS	=	Absorbance
nm	=	Unit for wavelength of absorbance

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

A widely used color considered to be natural is caramel color. By regulation, caramel is the amorphous, dark brown material resulting from the carefully controlled heat treatment of food-grade carbohydrates. D.D. Williamson is leading supplier of caramel color, and along with Sethness, has been producing it for more than 100 years. Caramel colors provide a wide range of stable colors for use in foods and beverages, from light yellows to red-browns to very dark browns, and it can be in the form of liquid or solid depending on the specific color and level of use (Kathie, 2010).

The first and commercial caramel was produced in Europe about 1850 by heating sucrose in an open pan. In industry, caramel is produced by controlled heating of carbohydrate source, in a process called, caramelization (Pintea, 2007). The caramelization reaction occurs at high temperatures in the presence or absence of catalysts which are acids, basis, salts or impurities (Quintas et al., 2007). The example of carbohydrates used as raw material are glucose syrups, sucrose, fructose, and dextrose (Kamuf et al., 2003). Most caramels, however, are being prepared from corn syrup (Benhura et al., 1999).

Demands of the caramel quality improvement and controls as well as the market are increasing. Therefore color, stability and flavor are most important characteristics in applications (Tsai et al., 2009). In the production of caramels from the usual carbohydrate materials, the formation of color depends on the nature of the starting material, its concentration, temperature, pH and the nature of catalysts that may be used (Quintas et al., 2007). However, the chemical composition and caramel properties are depending on types of reactant used and technical conditions such as time, temperature, moisture content and pressure (Kamuf et al., 2003).

Caramel color can be used for many applications. It is mostly used in carbonated beverages, distilled liquors, pharmaceutical flavouring extracts, candies, soups and bakery products (Chappel & Howell, 1992; Light et al., 1992). It is especially popular in the beverage industry, but caramel colors also are prevalent in baked goods, meat products and texturized vegetable proteins. Caramel colors can be used to imitate special processes, such as the addition of grill marks, which may provide an added value to some consumers (Marcia, 2006).

In the USA, more than 80% of caramel is used to color drink such as colas and beers. Furthermore, it also use for the coloring of blended whiskey (Pintea,2007). Caramel color, from the palest yellows to the deepest browns, accounts for more than 80% (by weight) of all colorants added to the foods we eat and drink. Annual global consumption exceeds 200,000 tons (Kamuf et al., 2003).

1.2 Caramelization

Caramelization is a process of sugar turning brown when heat is applied. During this process, water is being removed from the sugar (Kamuf et al., 2003). The caramelization process can be conducted in open or closed vessels. The mixture obtained is cooled and filtered, and then the ph and specific gravity are adjusted by the addition of acids, alkalis, or water (Pintea, 2007). Caramelization causes

important changes in foods, not only in color but also in flavor. As no enzymes are involved in the caramelization process, it is a non-enzymatic browning reaction. During a caramelization reaction, the sugars initially undergo dehydration and then condensation or polymerization into complex molecules of varying molecular weights. Lightly colored, pleasant-tasting caramel flavors are produced during the initial stages, but as the reaction continues higher molecular weight color bodies are produced, and the flavor characteristics become more bitter (Kamuf et al., 2003).

1.3 Classes of caramel

There are, in fact, four distinct types of caramel color to satisfy the requirements of different food and beverage systems.

Table 1.1: Classification of caramel classes

Class	Description	Restriction of preparation	Used in
I	Plain caramel, caustic caramel, spirit caramel	No ammonium or sulfite compounds can be used	Whiskey among many
II	Caustic sulfite caramel	In the presence of sulfite compounds but no ammonium compounds can be used	
III	Ammonia caramel, baker's caramel, confectioner's caramel, beer caramel	In the presence of ammonium compounds but no sulfite compounds can be used	Beer, synthetic soy sauce, and confectionery
IV	Sulfite ammonia caramel, acid-proof caramel, soft-drink caramel	In the presence of both sulfite and ammonium compounds	Acidic environments such as soft drinks

Each type of caramel color has specific functional properties that ensure compatibility with a product and eliminate undesirable effects, such as haze, flocculation, and separation (Kamuf et al., 2003).

1.4 Problem Statement

Caramel colors are the most widely used food coloring agent found in a wide range of food and beverages. So, it is important to produce caramel with good quality.

For caramel color, the most important properties are the color intensity. From the color intensity, the quality and the class of the caramel can be obtained. So it is important to study about the color intensity

The color intensity affected by pH, types of catalyst and also the preheating temperature. Good color intensity can be obtained when the best pH, preheating temperature and catalyst types are used.

1.5 Objectives

a) To investigate the effect of catalyst types on caramel preparation.
b) To study the effect of pH and preheating temperature for caramelization process.
c) To specify the time required to complete the process of caramel preparation.

1.6 Scope of Study

To achieve the objectives, scopes have been identified in this research as follow:

a) Use glucose as a carbohydrate to produce caramel color
b) To investigate the effect of catalyst for caramel production, two types of catalyst are used which is Ammonia and Ammonia with Sodium sulfite
c) The pH solution use for caramelization ranged from 5 to 9.
d) The temperature for preheating ranged from 70°C to 100°C

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

According to FDA (Food and Drug Administration), 'the color additive caramel is the dark brown liquid or solid that resulting from the carefully control treatment of the carbohydrates compound. JECFA define caramel as a complex mixture of compound, some of which are in the form of colloidal aggregates, manufactured by heating carbohydrates either alone or in the presence of food-grade alkali, acid or salt; classified according to the reactant used (Pintea, 2007).

In the past research, caramel color has been manufactured from food-grade carbohydrates and there is also a report about preparation of caramel from fruits extraction and also fruit wastes. The process used to produce it is by using caramelization. The caramelization process may be conducted in either open or closed vessels (Pintea, 2007).

From the research, it shows that there are a few factors that affect the production of caramel color. Caramelization product consists of volatile and non-volatile fractions of low and high molecular weights that vary depending on temperature, pH, time used for heating and starting material used (Defaye et al., 2000).

In the present work, studies will be conducted to determine the best condition of caramel color to get the high quality index of caramel color.

2.2 Manufacture of Caramel Color

Caramel color is produced and manufactured by heating carbohydrates raw material, at high temperature with or without reagents. The control of temperature, pressure, pH and reactant concentration also important to get desired product (Pintea, 2007; Kamuf, 2003; Meisel, 1969). A lot of research had been done to improve the quality of caramel color production.

Starting from 1943, William started to investigate about caramel color. In his research, he tried to use various sugar and Citric acid or Tartaric acid for caramelization at high temperature. First, Leomonade and Citric acid which containing high proportion of citric acid can undergo caramelization if stored in container at 98°F to 110°F. He found that under these conditions citric acid loses water of crystallization which brings about the hydrolysis of sucrose. The liberated fructose is then caramelized. Caramelization occurs with sorbose, fructose, or any sugar liberating fructose on hydrolysis. Aldohexoses and sugars liberating aldohexoses on hydrolysis do not caramelize in the presence of citric acid. Caramelization in orangeade and lemonade powders containing citric acid held at high temperatures can be prevented by using anhydrous citric acid or by substituting glucose for sucrose. Caramelization does not occur (in the absence of added water) if d-tartaric acid is substituted for citric acid.

Next, in 1950, Longenecker have invented method to produce caramel from hydrolysis product of starch that has stability in acid solution. He used corn syrup as a raw material and succeeded to get caramel that have stability in acid solution which is pH above.

Then, Meisel improved the preparation of caramel color by conducted it using starch hydrolyzate as a raw materials and ammonium bisulfite as reagent in continuous process that having dextrose equivalent (D.E) of 78 % and density of 43° Bé. Meisel used his invention to obviate problems associated using batch processes. He succeeded to reduce the time to maintain the caramelization temperature at a period of 1 to 10 minutes (Meisel, 1969).

As Ammonia caramel used widely in food industry, Setlur and his friends invented a continuous fast cook process for production of Ammonia caramel color. In this process, ammonia caramel is produced by pumping a heated steam of corn syrup through reaction under pressure continuously at high temperature. To produce ammonia caramel, catalyst such as ammonia or ammonia hydroxide is added at plurality location under control condition and it showed that 4MeI and THI content is acceptably low and hazing is prevented.

Caramel color also can be produced from polysaccharide. It has been proven in the production of caramel color from polysaccharide material extracted from the fruit of Azanza garckeana with the presence of ammonium salts. The mucilage extracted from the Azanza garckeana with water, is heated at 130°C until the brown color (caramel) is formed (Benhura et al., 1999). The presence of ammonium chloride and ammonium sulphate enhance the development of caramel color while lower pH appeared to improve the caramelization (Setlur et al, 1983)

In some cases, it is also possible to prepare caramel color from fruit wastes. Several researches has been done and Umerie find that the sugary saps of African oil palm exuded from the base of cut spathes of the oil palm and wine palm trees are analyzed and processed into caramel by acid-heat treatment in the presence of ammonia (anhydrous). The acid-heat treatment used to affect dehydration and polymerization of the sugars in the samples (Fetzer, 1964). The addition of ammonia (anhydrous) with continuous heating gives the desired product of concentration between 30-40° Bé. The use of sugary saps reduces cost and increase the availability of caramel. In particular applications; the food-colorant industry and the tobacco industry, the desired product in caramel color manufacture is the polymeric material and not the numerous volatile and semi-volatile compounds formed in such reactions (Lauterbach et al., 2002). The polymeric material is formed from the reactions of reducing sugars with ammonia and ammonium salts in Parr bomb at 93°C for 2.5 h.

2.3 Caramel Classes

Caramel colours have been classified into 4 classes which differ in their method of manufacture, composition, functional properties, and application. Kamuf and his friends have been discussed about catalyst used for caramel color. The catalyst can be used for caramel are sulphite and ammonia compound which is depends on the classes. Different caramel classes use different catalyst. For ammonia, the compound that can be used are hydroxide, carbonates, sulfites, bicarbonates, phosphate, sulphate and bisulphate. The sulfite compound that can be used are sulforus acid and sulphites, and bisulfites of potassium, sodium and ammonium. They also studied about the limits for caramel color. The limits for all classes are not more than 3 ppm of arsenic, not more 10 ppm of lead and not more than 0.1 ppm of mercury (Kamuf et al., 2003).

When trying to determine which of the four caramel colors will work best in certain applications, it is important to test tinctorial power (a measure of color strength), pH and Baume (a measureof liquid density or solids level). Adding a caramel color with the wrong ionic charge can cause color precipitation, flocculation or migration problems. Class III caramels have a positive charge, and Class II caramels have a strong negative charge. It is possible to blend Class I, II or IV and not have an ionic haze or precipitation. According to Geerts, when caramel colors are being used to match the appearance of another product, it is also necessary to examine taste and odor. The ammonia in Class III produces more flavor components, which can cause a chocolate or coffee-like flavor. On the other hand, Class IV is mild and typically used as a cola caramel. Many processors are interested in Class I caramels because they are considered to be more natural compared to the other caramel classes. However, they have low color strength, and manufacturers tend to use more of them to increase the color strength. Unfortunately, Class I also has a strong bitter aftertaste, which can be doubled during an attempt to increase color strength. But, certain caramel coloring companies offer a Class I caramel that does not have a strong bitter aftertaste (Marcia, 2006).

(a) (b) (c) (d)

Figure 2.1: Example of color for caramel classes (a) Class I, (b) Class II, (c) Class III, and (d) Class IV

2.4 Effect of Parameter

The chemical properties and composition of caramel color depends on reactant used and technical condition such as time, temperature, moisture content, pressure, concentration, pH and the nature of catalysts that may be used. (Pintea, 2007; Benhura, 1999). The time required for caramelization is different depends on the quality of caramel color desired. The time for caramelization in open pan is longer than in closed pan (Meisel, 1965).

In 1995, Diaz and Clotet study about the kinetics of caramelization for several monosaccharide and disaccharide. From the study, they found that at temperature 75°C to 95°C browning rapidly increase with time and to a higher final value with increasing temperature. This effect being more marked on monosaccharide compared to disaccharide.

The effects of pH, sugar and temperature on caramelization, was evaluated by Park et al., (1998). In this study, they found that the highest rate of reaction is fructose followed by sucrose. As reaction temperature increase from 80°C to 110°C, reaction rate was greatly increased proportionally while the optimum value for pH is determined as 10.

Meisel in his study found that temperature used to produce caramel color cannot be too high because it will destroy the quality of caramel. Maintaining the pH at low value may facilitates the effect of caramelization on sugar liquor (Longenecker, 1950). Hence, it has been proven that caramel color has good functionality across a wide range of from 2 to 10. Most caramel color ranges from 2 to 5 but as for caramel color that has been neutralized prior to spray drying; the pH is found to be 8. Commercial liquid caramel color should posses a pH of 5 to provide good stability.

Although caramelization is favored at high temperature than 120°C pH less 3 and greater than 9, depending on the composition of the system (pH and types of sugar), caramelization reaction also can occur at in system heated at low temperature. Thus, some studies have been conducted at temperature 45°C to 65°C with ph 4-6. The author studied about the changes of color due to the different types of sugar used (fructose, xylose, glucose, maltose, lactose and sucrose) in model system 0.9 $a_{w.}$ from the experiment, he found that fructose and xylose browned much more rapidly compare to other sugar and that lowering the inhibited caramelization browning of sugar solution (Buera et al., 1987).

In a reaction between reducing sugar and with ammonia and ammonium salts, the major reaction product is 2, 6-deoxyfructosazine. In this particular study, dextrose is reacted in aqueous solution with each of the following ammonium salts: acetate, bicarbonate, carbonate, chloride, citrate, formate, monohydrogenphosphate (DAP), sulfate, and sulfite. The initial pH of all reactions is set at 8. The results show that among the ammonium salts typically used for ammoniation of glucose, DAP has enhanced reactivity, and this reactivity is likely due to the fact that the monohydrogenphosphate anion can act as both an acid and a base.

2.5 Mechanism of Caramelization

In a Greenshields & Macgillivray study, they find that in the production of caramel color the degradation of carbohydrates involves a number of competing and consecutive reactions that are accelerated at high temperatures and are catalysed by acids and bases. Caramelization reactions include changes in the ring size of monosaccharides, breakage and reformation of glycosidic bonds, dehydration, introduction of double bonds and the formation of anhydro rings. The formation of colour could also arise from oxidation reactions that involve ascorbic acid.

The French chemist, M. A. Gelis indicated that caramelized sucrose contains three main products: a dehydration product, caramelan $C_{12}H_{18}O_9$; and two polymers, caramelen $C_{36}H_{50}O_{25}$ and caramelin $C_{96}H_{102}O_{51}$. Greenshields indicated that it is common for both Maillard and caramelization reactions to yield aldehydes and dicarbonyl compounds, but the former reaction incorporates nitrogen-containing components.

For this case, Hodge and Greenshields grouped the reaction mechanisms as follows:

1) Starting reactions
    a) Sugar-amino condensation
    b) Amadori or Heyns rearrangement

2) Degradative reactions causing the formation of colorless or yellow products with strong ultraviolet absorbance and the release of carbon dioxide
    a) Sugar dehydration
    b) Ring splitting (Strecker degradation)

3) Polymerizing or condensing reactions forming strongly colored components of relatively high molecular weight
    a) Aldol condensations
    b) Aldehyde/amino polymerization and formation of heterocyclic nitrogen compounds

In other study, Kroh found that caramelization comprises the reactions involved in the thermal decomposition of carbohydrates, in particular reducing monosacharides and disaccharides. Various stages of the caramelization reaction may be discerned. The first step in most caramelization reactions involves internal reorganizations with the carbohydrates which are known as enolizations. The second step comprises the formation of the anhydro form of the carbohydrate via the elimination of a water molecule. This is followed by variety of chemical reactions which depend strongly on the precise sugar composition, sample conditions like pH and the temperature. In these intermediate stages, most of the volatile compounds associated with caramel flavor are formed. In a fairly late stage of the caramelization reaction, brown-colored polymeric substances are formed via radical polymerizations. The caramelization of carbohydrate polymers and their mixtures with low-molecular-weight sugars is of interest for food processing not only because of the caramel flavor and color, but also because the changes in sugar structure and the liberation of water during the caramelization reaction could have a potentially significant effect on the mechanical and barrier properties of the carbohydrate system. In particular, the water liberated during caramelization could decrease the glass transition temperature of the amorphous carbohydrate matrix (Kroh, 1994).

2.6 Characterization of Caramel Color

Caramel flavoring and coloring, produced from sugar with different catalyst, known as the most widely used in food industry. However, caramel is not always desirable reaction due to the possible formation of mutagenic compound and the excessive changes in the sensory attributes that could affect the quality of the quality of certain foods.

During the manufacture of caramel color, unsaturated reactive species created by the dehydration of carbohydrates polymerize to form high molecular weight constituent (HMW) (Myers & Howell, 1992). Low-molecular weight (LMW) products are also formed by degradative reactions. The compound used as markers are 5-hydroxymethyl-2-furaldehyde (5-HMF, which is present in all four caramel

classes (Francisco and Octavio, 2000). Among the LMW products detected in the four classes of caramel color are 5-(hydroxymethyl)-2-furaldehyde (5-HMF), 4-methylimidazole (4-MeI) and 2-acetyl-4-(1,2,3,4-tetrahydroxybutyl)imidazole (THI). The compound 5-HMF has been detected in all four classes of caramel while the compound 4-MeI has been detected in Class III and Class IV caramel colors but not in class I and II caramel colors (Licht et al., 1992).

Caramelization is catalyzed under alkaline or acidic conditions. In 1976, a research had been done by Fenemma to a various types of sugar, and he found that in acid media, low amount of isomeric carbohydrates are formed. However, dehydration is favored leading to the formation of furaldehyde compound; 5-(hydroxymethyl)-2-furaldehyde (5-HMF) from hexose and 2-furaldehyde from pentose. With unbuffer acid as catalyst, higher yield of HMF are produced from fructose than glucose. Also only the fructose moiety of sucrose is largely converted to HMF under the unbuffre condition that produced highest yield. The enolization of glucose can be greatly increased in buffer acidic solution. Thus, higher yield HMF are produced from glucose and sucrose when a combination of phosphoric acid and pyridine is used as catalyst than phosphoric acid is used alone.

Then, in 1998 Laura done the test for 10 commercial caramel color (I, II, III and IV). and suspect caramel. 4-MeI was detected in all class III and IV but not in class I and II. Major coeluting interferences completely precluded the analysis for 5-HMF and THI in all of the class III and one of the class IV caramels. However, 5-HMF was detected in all of the remaining caramel colors tested including the class I, class II, and class IV caramel colors and the suspect caramel color; THI was not detected in any of these caramel colors. For the determination of 4-MeI, the researcher observed the least interference from the class IV caramel colors, both because of higher levels of 4-MeI and less coeluting material. For the determination of 5-HMF and THI, major interferences were observed for all of the class III and one of the class IV caramel colors. Interferences were minimal for all other caramel colors tested including the supect caramel color (Laura, 1998)

A research has been done to analyze the THI compound in Class III caramel color using a simpler and faster way (Moretton et al., 2008). Heart-cutting two-dimensional liquid chromatography is used without any extraction step and with UV detection and proposing it to be fully automated procedures. The analysis results show that only a few of the samples corresponds to European limit of the THI concentration in foods. The samples were analyzed for about 30 minutes each in this analysis (Moretton et al., 2008). Determination of other caramel color markers can be determined using the same method proposed earlier.

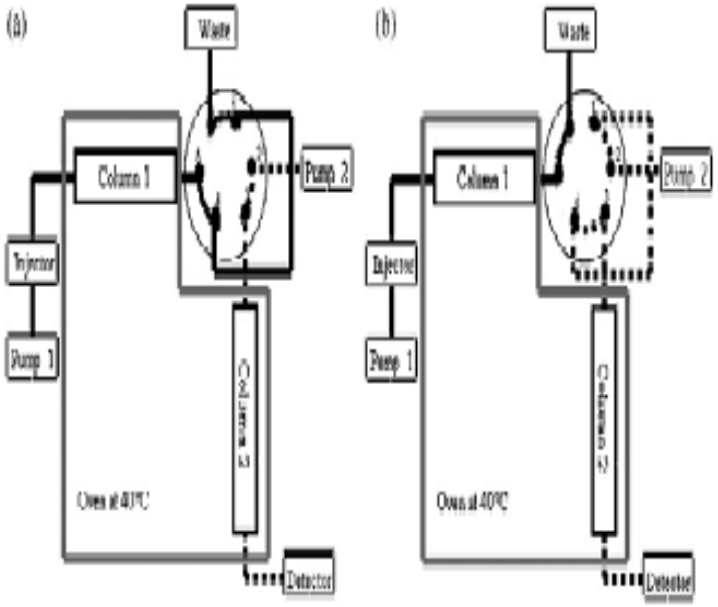

Figure 2.2: Experimental device for heart-cutting two-dimensional liquid chromatography (a) First-dimensional separation and heart-cutting (b) second-dimensional separation and detection (Moretton et al., 2008)

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

In order to achieve the outlines of the objectives and the scope of the study, several materials, experimental procedures used in this study are presented and discussed with more details in the following sections. The effect of pH, temperature and catalyst is the main target in achieving the objectives of this study. The materials and methodology used in this study are referred from the literature studies.

3.2. Chemicals

The chemicals used in this study were used for sample preparation. For preparation of caramel class III, ammonia solution with 25% concentration was used. And for preparation of caramel class IV, ammonia solution was used with addition of sodium sulfite. To adjust the pH of solution, hydrocloric acid and sodium hydroxide was used. Ammonia solution, sodium sulfite, hydrocloric acid and sodium hydroxide are provided by '*store 3*' at Faculty of Chemical and Natural Resouces Engineering. For carbohydrate, glucose was used for this research is bought from '*Tunas Manja*' manufactured by IDS Manufacturing Sdn Bhd.